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Exchange Reactions as a Basis of Thermoplastic Behaviour in Crosslinked Polymers

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An attempt has been made to achieve thermoplastic behaviour in a chemically crosslinked elastomer by arranging that the crosslinks should undergo rapid exchange at high temperatures. Natural rubber was chemically modified to give pendent hydroxyl groups which were then used as crosslinking sites to form β-keto-ester or malonate crosslinks. The resultant vulcanisates showed high stress relaxation rates in the temperature range 120 to 160 °C and some degree of remouldability at 180 °C. The incursion of permanent crosslinking prevented. quantitative correlation between stress relaxation rates and chemical exchange rates of the crosslinking systems.

1. Introduction

Block copolymer rubbers, e.g. styrene–butadiene–styrene block copolymers, offer in some degree the elastic properties of conventionally crosslinked rubbers coupled with the direct thermal processability characteristic of plastics.[1,2,3] The block copolymers derive their elastic properties at ambient temperature from the association of the segments of glassy polymer into domains which form a disperse phase in the matrix of rubbery segments. The glassy domains act as junction points between the rubber segments and provide a three dimensional network. Above the glass transition temperature of the glassy polymer the whole mass becomes plastic, and can be remoulded.

We have been investigating the possibility of conferring thermoplastic properties on highly elastic systems by introducing specific chemical crosslinks which are capable of undergoing rapid exchange at high temperatures. The general principle may be illustrated with reference to the phenomenon of chemical stress relaxation.

If a rubber network is held under stress by a force F and the crosslinks are broken one by one the stress will decay eventually to zero and the rubber chains will assume random coil configurations in the new physical shape (Figure 1). If the crosslinks can reform at new sites on the chains the network will finish up with a full complement of crosslinks and under zero stress, but with a new shape. The whole sequence can be

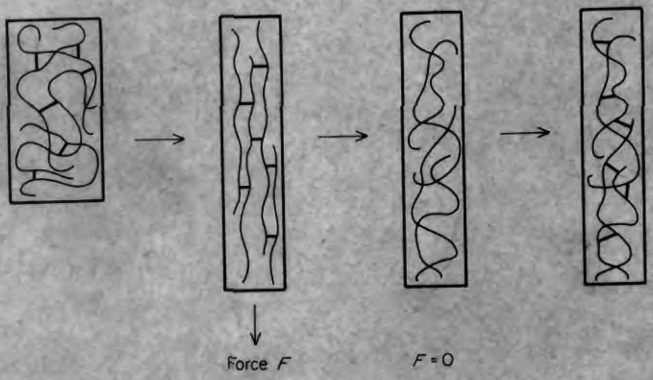

Figure 1. Schematic representation of the stress relaxation–crosslink recombination sequence for remoulding.

considered as a remoulding experiment in slow motion and it seems logical that as the rates of the crosslink breaking and re-formation (crosslink exchange) processes increase, the time required to remould the network will decrease. If the exchange rate is sufficiently high remoulding would be expected to take place in a practically useful space of time.

This paper reports our work on one particular exchanging crosslink system – the uncatalysed alcoholysis of β-keto-esters and malonates – and discusses the extent to which rubber networks based on crosslinks of this type have shown promise of thermoplastic behaviour.

2. Experimental

Details of the chemical investigations of model compounds will appear elsewhere. Rubber mixes were prepared by conventional procedures on a small two-roll mill and vulcanisate sheets (1 mm and 0.5 mm thick) were prepared by compression moulding. The peroxide vulcanisates were cured for 20 min at 100 °C followed by 2 h at 150 °C. The ester vulcanisates were cured for 60 min at 50 °C followed by 30 min at 140 °C; curometer traces showed that crosslink insertion did not increase over a further hour at 140 °C.

The stress relaxation apparatus consisted basically of an upper clamp mounted on a cantilever spring and a lower adjustable clamp to provide extension. Strain gauges were mounted on the upper and lower surfaces of the spring, forming two arms of a Wheatstone bridge. The out of balance voltage on the bridge, caused by deflection of the spring on extension of the rubber, was monitored continuously on a chart recorder. The apparatus was enclosed in a glass jacket and maintained at 10^{-3} mmHg by continuous pumping.[a] The apparatus was heated in a thermostatically controlled

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[a] Throughout this paper 1 mmHg ≈ 101.325/760 kN/m^2, 1 lbf/in^2 = 6890 N/m^2.

cylindrical electric oven, and the temperature was monitored by a thermocouple situated immediately adjacent to the rubber sample.

Hydroxylated NR was prepared as follows. Extracted NR (87 g, 1.28 mol of double bonds) was dissolved in chloroform (2 l) and the solution was cooled to − 40 °C. A solution of *m*-chloroperbenzoic acid (19.6 g, 0.106 mol allowing for 94% purity) in chloroform (300 ml) was added over 30 min with vigorous manual stirring. The reaction solution was allowed to warm to room temperature and after 1 h the rubber was precipitated with methanol. The rubber was purified by three further precipitations from chloroform and dried to constant weight (86 g). The dry rubber was dissolved in dry xylene (2.5l) and the solution was deoxygenated by repeatedly evacuating the flask on the water pump and filling it with nitrogen. Aluminium isopropoxide (70 g) in xylene (500 ml) was added with stirring and the flask again evacuated and filled with nitrogen. The flask was heated in an oil bath at 130 °C (solution temperature 120 °C) for 90 h. The cooled gel was treated with acetyl acetone (100 ml) to form the soluble aluminium complex and the rubber was precipitated with methanol and purified by three further precipitations from chloroform. The hydroxyl level on the modified polymer was 5.9 mol per 100 mol of double bond, representing 65% yield on the basis of the peracid used.

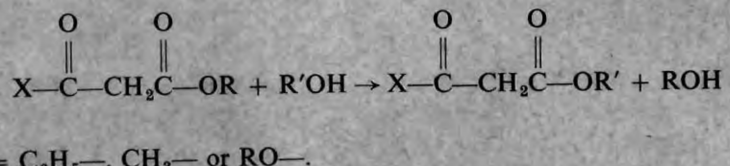
3. The exchange system

Construction of a rubber network whose crosslinks undergo rapid exchange would not, in itself, be sufficient to provide a practical thermoplastic system. If rapid exchange occurred at ambient temperatures the system would show very high creep and stress relaxation under service conditions. One of the essential characteristics of a suitable crosslink exchange reaction is that it should have a high activation energy, providing a large differential between crosslink exchange at high temperatures and crosslink stability at ambient temperatures.

The exchange process must also proceed smoothly in the rubber environment which, generally speaking, is non-polar and it must be free from any side reactions which give rise to permanent crosslinks on a time scale comparable with the exchange process.

In addition to these qualitative criteria, a thorough understanding of the kinetics and mechanism of the reaction of low molecular weight model compounds under appropriate solvent conditions would greatly assist the interpretation of the results of remoulding and high temperature stress relaxation experiments.

The reaction which we have investigated[4] is the uncatalysed exchange of alcohol groups on β-keto- and malonate esters:



$$X{-}\overset{\overset{O}{\|}}{C}{-}CH_2\overset{\overset{O}{\|}}{C}{-}OR + R'OH \rightarrow X{-}\overset{\overset{O}{\|}}{C}{-}CH_2\overset{\overset{O}{\|}}{C}{-}OR' + ROH$$

where X = C_6H_5—, CH_3— or RO—.

The general reaction was described by Carroll[5] who reported the reactivity sequence benzoylacetate (X = C_6H_5—) > acetoacetate (X = CH_3—) > malonate (X = RO—
The acetoacetate reaction was also studied by Bader and Vogel[6] who suggested that enolisation and internal hydrogen bonding played an important part in the mechanism. The exchange of malonate esters with 3-methylbutanol-1-ol, using the alcohol as solvent has been reported by Rowland *et al.*[7]

On the basis of initial reaction rates, the reaction of ethyl acetoacetate with propanol in heptane solution is first order in ester and independent of alcohol concentration, but the position of equilibrium is dependent on the relative amounts of reactant and product alcohols. The reaction rate is not markedly affected by change in polarity of the solvent, reaction in heptane being 3 times faster than in acetone, and 2.3 times faster than in propanol. The reactions of ethyl benzoylacetate and diethyl malonate with propanol show similar kinetic characteristics. Table 1 summarises some of the kinetic data for reaction of the three ethyl esters (0.100 M) with *n*-propanol (0.200 M) in heptane solution. The initial first order rate constants (k_1^1) at 180 °C are calculated from the measured activation parameters in the temperature range 90 to 130 °C. The half lives ($t_{\frac{1}{2}}$) at 180 °C are calculated without allowance for the fact that the reaction reaches equilibrium in solution.

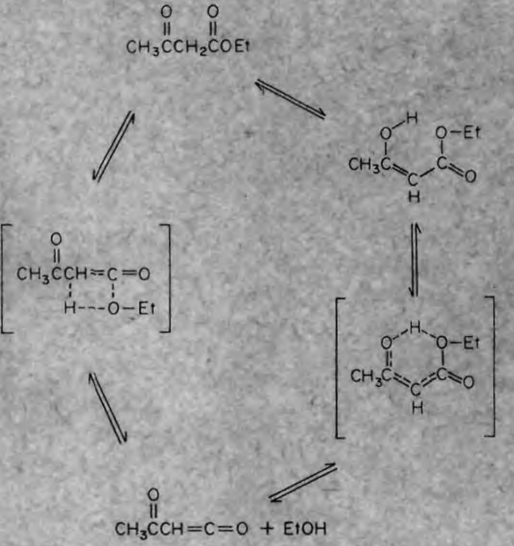
TABLE 1. Kinetic data for the exchange reaction in heptane solution

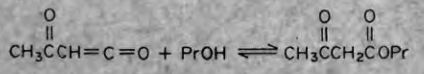
$$X.CO.CH_2CO.OEt + n\text{-}PrOH \rightleftharpoons X.CO.CH_2CO.OPr + EtOH$$

X	C_6H_5–	CH_3–	EtO–
k^1_1 at 110 °C (sec^{-1})	90×10^{-5}	12×10^{-5}	0.68×10^{-5}
$\Delta H\ddagger$ (kcal mol^{-1})	—	27 ± 2	26 ± 2
$\Delta S\ddagger$ (cal deg^{-1} mol^{-1})	—	-7 ± 5	-14 ± 5
k^1_1 at 180 °C (sec^{-1})	—	40×10^{-3}	1.5×10^{-3}
$t_{\frac{1}{2}}$ at 180 °C (sec)	—	17	460

There is a 150-fold increase in reactivity from malonate to benzoylacetate with acetoacetate lying conveniently in the middle of the range. The activation enthalpies for malonate and acetoacetate are high, and in conjunction with the numerically small negative entropies give a high dependence of reaction rate on temperature.

As a result of our studies in this reaction we have proposed a mechanism[4] which involves slow cyclic elimination of alcohol either via a four centre process from the keto-form of the ester or via a six centre process from the enol form to give a substituted keten as a reactive intermediate. The keten then reacts rapidly with the reactant alcohol to give the exchanged ester, or with the product alcohol to reform the starting ester (Scheme 1). The first order reaction rate is determined by the slow elimination process but the final position of equilibrium is governed by competition of the reactant and product alcohols for the keten intermediate.





$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH{=}C{=}O + PrOH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OPr}$$

Application of the β-keto-ester exchange reaction to the crosslinking of polymers can be done either by providing pendent β-keto-ester functions on the polymer chain and using a diol as the crosslinking agent or by providing pendent hydroxyl groups and using difunctional esters as crosslinking agents. The latter approach involves modification of the polymer with a relatively simple functional group, and was the approach adopted in the present work.

Malonate esters are inherently difunctional in the ester exchange reaction and can be used directly as crosslinking agents. A difunctional analogue of acetoacetate is available in the form of esters of acetonedicarboxylic acid (RO.CO.CH_2CO.CH_2CO.OR). In this type of ester, the central ketonic carbonyl group provides the activation for both ends of the molecule. The initial first order rate constant (k^1_1) for reaction of diethyl acetonedicarboxylate with *n*-propanol in heptane solution at 110 °C is 9.5×10^{-5} $\mathrm{sec^{-1}}$, in reasonably good agreement with the value of 12×10^{-5} $\mathrm{sec^{-1}}$ obtained for ethyl acetoacetate under the same conditions.[a]

A further factor which requires consideration in constructing the crosslink system is the fact that an equilibrium will be established between polymer-bound alcohol and alcohol liberated from the crosslinking ester. In order to ensure high crosslink yields, the liberated alcohol must either be removed from the system or must have a chemical reactivity such that it does not compete with the polymer alcohol for the keten intermediate. The latter situation can be achieved by using the diphenyl esters as crosslinking agents.

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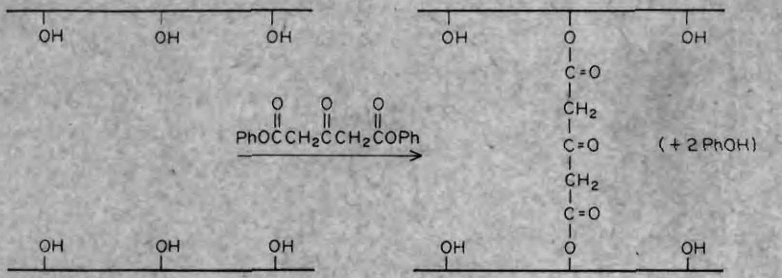
[a] In comparing rate constants for malonate and acetonedicarboxylate reactions with those for monofunctional esters, a statistical factor of two has been taken into consideration.

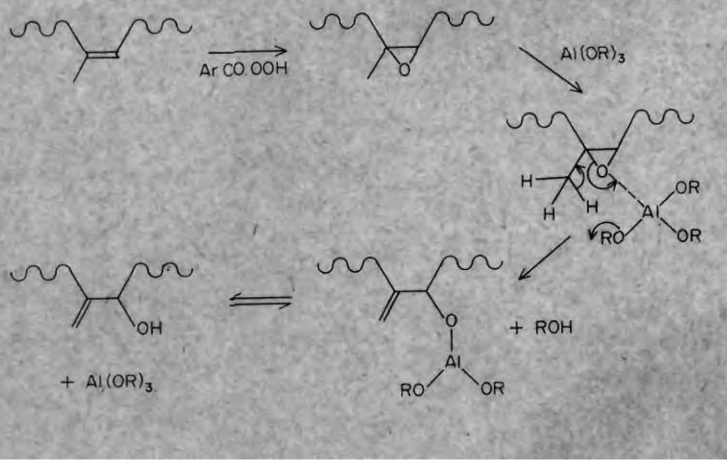
The crosslinking reaction is shown in Scheme 2 for the case of diphenyl acetonedicarboxylate. The liberated phenol plays no part in the system after initial crosslink formation. The exchange reaction occurs between the crosslink and excess polymer bound hydroxyl groups.



4. The modified polymer

We are primarily interested in the application of the ester crosslinking system to natural rubber (NR) and we have therefore concentrated our efforts on the modification of NR to give pendent hydroxyl groups. A number of attempts to use 'ene' reactions[8] and 1,3-dipolar addition reactions[9] to provide the required modification were unsuccessful. Using the former reaction type, difficulties have been encountered in obtaining a hydroxyl-containing reagent of suitable reactivity, and with the 1,3 dipolar addition reaction, the response of trialkyl ethylenes is generally sluggish, giving poor yields of bound hydroxyl groups.

We have obtained experimental quantities of hydroxylated NR via the reaction sequence summarised in Scheme 3. A limited proportion of the double bonds in the polymer were epoxidised using *m*-chloroperbenzoic acid in chloroform solution. The solutions of peracid and rubber were mixed at − 40 °C to ensure the formation of a homogeneously epoxidised product. The epoxidised rubber was then heated for 90 h



at 130 °C in xylene solution with aluminium isopropoxide to give isomerisation to the allylic alcohol.[10–13] The level of hydroxyl groups in the modified rubber was estimated by benzoylation of the rubber in pyridine solution and comparison of the intensities of the aromatic C—H and the aliphatic CH_2/CH_3 absorptions in the infrared, using an ethyl benzoate/squalene calibration curve.[14] The rubber contained 5.9 hydroxyl groups for every 100 isoprene units, i.e. 8.7×10^{-2} mol per 100 g of rubber. This represents an overall yield of 65 % based on the amount of peracid used.

The hydroxylated NR had a molecular weight of approximately 160000, based on the viscosity–molecular weight relationship for NR.[15] It should be pointed out, however, that the presence of the hydroxyl groups is liable to have a substantial effect on this relationship, and since the dry rubber was soft and sticky a molecular weight of 100000 was assigned for the purpose of calculating crosslink densities of vulcanisates. Elaborate efforts to exclude molecular oxygen from the reaction system did not eliminate the drop in molecular weight, suggesting that a certain amount of chain scission was associated with the isomerisation reaction.

5. Preparation and characterisation of the vulcanisates

Several vulcanisates were prepared from the hydroxylated NR by conventional milling and pressing techniques. Table 2 gives details of three cures prepared with carefully matched crosslink densities to facilitate comparison of their behaviour in remoulding and stress relaxation experiments. The crosslinking agents used were dicumyl peroxide (DICUP), to give a control vulcanisate permanently crosslinked with carbon-carbon bonds, diphenyl acetonedicarboxylate (DPA) and diphenyl malonate (DPM). Antioxidant 2246 (substituted phenol) was incorporated in the two ester cures.

The chemical crosslink densities of the vulcanisates were determined by Mooney–Rivlin stress–strain analysis and application of the Moore–Mullins–Watson calibration of elastic constant C_1 and chemical crosslink density.[16] The crosslinking efficiency for the malonate cure was 68 % but for the acetone dicarboxylate cure it was only 43 %.

Samples of the freshly prepared ester vulcanisates were heated in a mixture of *n*-butanol and xylene (1:3) at 110 °C for 48 h. The acetone dicarboxylate sample dissolved completely, indicating that all the crosslinks were of the exchangeable ester type. Approximately 50 % of the malonate sample dissolved. The remainder formed an extremely highly swollen gel, indicating that a very small number of permanent crosslinks were present.

TABLE 2.

Curing reagent	Wt. of rubber (g)	Wt. of reagent (g)	Wt. of 2246 (g)	10^4 [Diphenyl ester] in mix (mol/g RH)	10^{-6} C_1 (dyn/cm^2)	10^{-6} C_2 (dyn/cm^2)	10^4 $(2M_c \text{ chem})^{-1}$ (mol/g RH)
DICUP	5	0.060	—	—	1.38	0.57	0.47
DPA	5	0.102	0.05	1.00	1.25	0.63	0.43
DPM	6.1	0.102	0.05	0.65	1.29	0.75	0.44

Press remoulding at 180°

Transfer remoulding at 180°

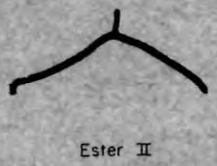


Figure 2. Remoulded samples of carbon–carbon crosslinked ($\geqslant$ C–C $\leqslant$), malonate crosslinked (Ester I) and acetonedicarboxylate crosslinked (Ester II) vulcanisates.

6. Remoulding and stress relaxation

The results of a number of qualitative remoulding experiments are shown in Figure 2. The samples at the top of the figure were obtained by placing pieces of each of the three vulcanisates (approx. 1 × 1 × 0.1 cm) in a press at 180 °C and 4500 lbf/in^2 for 5 min. The peroxide cured sample (carbon–carbon crosslinks) broke into small crumbs whereas both ester crosslinked rubbers were recovered as distorted discs. The malonate sample (Ester I) contained a number of very large tears whereas the acetone dicarboxylate sample (Ester II) was completely coherent. The general trend in behaviour of the three vulcanisates was in the order of expected change in crosslink mobility (C–C $\ll$ malonate $<$ acetonedicarboxylate), but the fact that an undistorted film could not be obtained, even with the acetonedicarboxylate rubber, shows that the remoulding process did not go to completion. Increasing the time that the samples were in the press at 180 °C did not improve the quality of the remoulding.

Samples of the vulcanised rubbers were also passed through a small transfer mould at 180 °C. All three rubbers passed through the orifice as small crumbs and in the case of the peroxide cure these gave no subsequent cohesion. In the case of the acetonedicarboxylate cure, cohesion to give a remoulded sample did occur (Figure 2) but the sample became distorted on removal from the mould and tended to tear preferentially along the visible crumb boundaries. The malonate cure gave a remoulded sample

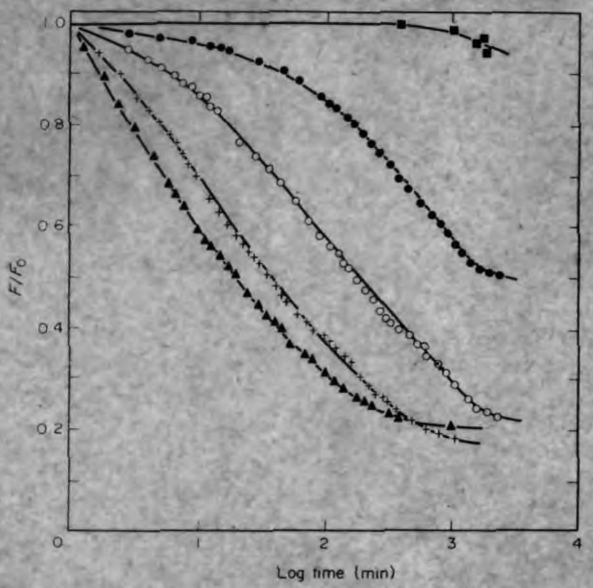


Figure 3. Stress relaxation results: Carbon–carbon (■), malonate (●) and acetonedicarboxylate (▲) vulcanisates at 158 °C; acetonedicarboxylate vulcanisate at 143 °C (+) and 122 °C (○).

similar to the acetonedicarboxylate one but with considerably less resistance to tearing.

The stress relaxation behaviour of the vulcanisates was studied in the temperature range 120 to 160 °C *in vacuo*. The results are summarised in Figure 3 in terms of stress, relative to the initial stress, versus log time. The peroxide cured rubber showed no significant loss of stress over the first three decades of time at 158 °C, indicating that physical relaxation processes were not significant on the time scale of these experiments. In general terms, the relaxation rates for the two ester cures at 158 °C were in the order of expected crosslink mobility (acetonedicarboxylate > malonate) but both cures gave an extremely small relaxation rate after three decades of time. The level of residual stress at which relaxation became negligible was 20% for the acetonedicarboxylate cure and 50% for the malonate cure. The relaxation rate of the acetonedicarboxylate cure decreased with decreasing temperature, but the residual stress level at which relaxation became negligible remained near 20%.

On the basis of the kinetic work on model compounds, the crosslink exchange process in the ester cures is expected to be first order in relation to the crosslink concentration and independent of the hydroxyl group concentration. Also, in the model systems, the keten intermediate does not accumulate to a spectroscopically detectable level,[4] which means that in the ester cures there should not be a significant proportion of the crosslinks in a dissociated form at any one time. The total number of crosslinks in the system should therefore remain constant with time and the relaxation process should occur via a kinetically first order randomisation of the crosslinks. Flory[17] has discussed this type of system from a theoretical viewpoint, and has proposed the relationship

$$kt = -\ln f/f_0 + \frac{(-\ln f/f_0)^2}{2.2!} + \frac{(-\ln f/f_0)^3}{3.3!} + \ldots\ldots$$

for stress relaxation at a fixed elongation. In the relationship f and f_0 are the force at time t and force at zero time respectively and k is the rate constant for the first order chemical exchange process. The relationship predicts that the stress relaxation curve will have an initial slope equal to the slope of the first order chemical reaction of rate constant k but the loss of stress will be progressively less than would be expected for a simple first order relationship. Flory describes this behaviour as arising from a 'memory imposed on the second stage crosslinkages by the primary network', i.e. crosslinks reforming at any given time do not necessarily do so in a situation which is completely relaxed relative to the state of the network at some later time. It follows that any particular crosslink may have to undergo a number of exchange steps before the network as a whole has reached full relaxation.

Flory's theoretical relationship is shown graphically in Figure 4, together with experimental results for the acetonedicarboxylate cure at 158 °C. The value of the rate constant k (7.4×10^{-3} sec^{-1}) for the acetonedicarboxylate crosslink exchange was calculated from the activation parameters for exchange of ethyl acetoacetate and propanol, with allowance for the fact that the rubber bound hydroxyl group is secondary and not primary.[a] The total time scale of Figure 4 is approximately 20 min. In this time, Flory's relationship would predict 95% loss of stress whereas the experimental results gave only 48% loss.

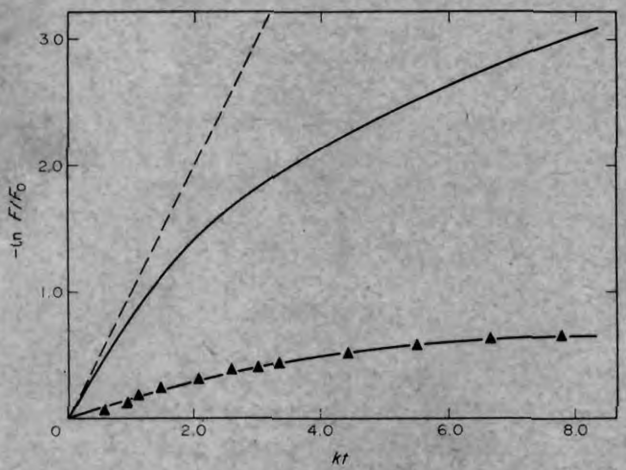


Figure 4. First order stress decay (- - - -), Flory relationship (——) and experimental stress decay for acetonedicarboxylate vulcanisate (▲) at 158 °C using $k = 7.4 \times 10^{-3}$ sec^{-1}.

There are a number of possible explanations for the discrepancy between theoretical prediction and the experimental results, At present, errors in the theoretical relationship will be discounted, but errors in its application may arise through the need for

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[a] The relative rates of reaction of ethyl acetoacetate and *sec*-butyl acetoacetate at 110 °C are 1:1.42.

assigning a value of the rate constant, k, for the chemical exchange process *in the rubber network*. Reduction of the assigned value of k by a factor of 10 would give agreement between the experimental and theoretical curves of Figure 4 over the first half of the relaxation but the experimentally observed loss of stress over 200 min (73%, Figure 3) still falls short of the predicted value of 95%.

None of the experimental relaxations attained complete loss of stress and it seemed probable that this was due to formation of permanent crosslinks during the relaxation process. This was confirmed by the fact that the rubbers were no longer soluble in butanol/xylene mixture at 110 °C at the end of the relaxation experiments. The theoretical treatment of Flory has been extended by Scanlan[18] to cover the case of first stage crosslink cleavage followed by irreversible recombination. Although this formally represents analysis of chemical stress relaxation accompanied by permanent crosslinking, we cannot be sure that our relaxation process follows the required stoichiometry of loss of one labile crosslink followed by formation of one permanent crosslink. We have therefore refrained from extending the mathematical analysis of the results in the hope of being able to eliminate the permanent crosslinking reaction.

An apparent activation energy of 5 kcal mol^{-1} for relaxation of the acetonedicarboxylate cure was calculated from the initial slopes of the $\log f/f_0$ versus time curves at 122, 143 and 158 °C. This is less than one fifth of the expected chemical activation energy for the crosslink exchange process. Taken in conjunction with the apparently low value of k in the relaxation process, it could be a reflection of a substantial degree of diffusion control of the chemical exchange in the rubber system.[a] Work on the effect of bound alcohol concentration on relaxation rate will be necessary to confirm or disprove this hypothesis.

7. Conclusions

The alcoholyses of β-keto- and malonate esters in hydrocarbon solution have rates and kinetic characteristics suitable for testing the concept of thermoplastic behaviour being achieved via crosslink exchange. NR networks can be constructed with crosslinks of these types, and at temperatures above 150 °C they show very high levels of stress relaxation compared with a conventionally crosslinked rubber. They also show some degree of remouldability but are prevented from achieving complete relaxation of remoulding stresses by the incursion of permanent crosslinks. The chemistry of the permanent crosslinking process has not yet been identified. Further work is being aimed at preventing this permanent crosslinking and obtaining quantitative correlations between chemical exchange rates and stress relaxation behaviour.

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[a] The author is indebted to a referee for raising this possibility.

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